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(54) Photosensitive composition

(57) Disclosed is a photosensitive composition comprising an *o*-quinonediazido compound and a novolak resin, wherein the *o*-quinonediazido compound is an *o*-naphthoquinone-diazidosulfonic acid ester of a polycondensation resin of pyrogallol with acetone and has a number-average molecular weight (Mn) of 5.0×10^2 to 1.5×10^3 and a weight-average molecular weight (Mw) of 7.0×10^2 to 4.0×10^3, and the novolak resin has a weight-average molecular weight (Mw') of 6.0×10^3 to 2.0×10^4 and the ratio of the weight-average molecular weight (Mw') to a number-average molecular weight (Mn') of the novolak resin (Mw'/Mn') is 2 to 14.

The photosensitive composition of this invention has improved resistance to an oily ball-point pen employing an organic solvent as solvent for ink and safelight property without reduction of sensitivity, has excellent property in under- and over-development, and has a wide development latitude.

SPECIFICATION

Photosensitive composition

BACKGROUND OF THE INVENTION

This invention relates to a photosensitive composition which shows superior safelight property, ball-point pen resistance and development latitude and is suitable for a positive type photosensitive lithographic printing plate and photoresist.

Photosensitive layers for the positive type photosensitive lithgraphic printing plate or photoresist usually contain an *o*-quinonediazido compound as a photosensitive component and an alkali-soluble resin as a component for enhancing film strength and solubility in alkali.

Where plural original films are to be in turn printed at varied positions onto a photosensitive lighographic printing plate having a photosensitive layer of such *o*-quinonediazido compound, i.e., the so-called "step and repeat printing doon", the position of original may be marked on the photosensitive layer in order to adjust positions of original films. In this instance, an oily ball-point pen is usually employed as a writing tool for said marking. However, if a solvent for ink in ball-point pen is an organic solvent, particularly, any high-boiling solvent of glycol type, etc., the photosensitive layer of a photosensitive lithographic printing plate tends to be attacked with said ink and dissolved in turn away. If the marked points are located in an image portion, there may be caused a disturbance wherein development of the plate as such may remove the photosensitive layer in the marked part in an image portion and the marked part may be reproduced on a printed matter when printed. Thus, there is desired a photosensitive lithographic printing plate having a photosensitive layer which is not susceptible to attack by ball-point pen ink (hereinafter referred to as "ball-point pen resistance").

Moreover, the photosensitive lithographic printing plate using said *o*-quinonediazido compound, when printing is worked under a white-color fluorescent lamp, may frequently undergo optical fog and, when subsequently developed, the photosensitive layer in image portion may be attacked to cause reduction in the layer and in printing resistance when printed. Thus, there is desired a photosensitive lithographic printing plate having a photosensitive layer with an improved resistance to optical fog by a white color fluorescent light (hereinafter referred to as "safelight property").

Further, development of a photosensitive lithographic printing plate or photoresist using *o*-quinonediazido compounds is usually effected with a developer of an aqueous alkali solution; however, developing capacity of a developer is apt to be altered under various conditions, developing capacity may be reduced owing to exhaust by processing in a large scale or deterioration by aerial oxidation and, eve if processed, the photosensitive layer of non-image portion in printing plate or photoresist would not be completely dissolved. Also, to the contrary, developing capacity tends to be raised beyond a standard level owing to an excessively replenished amount or raised bath temperature upon atmospheric temperature so that the image portion in the printing plate may be attacked or dots may disappear. Therefore, the photosensitive lithographic printing plate is particularly desired to have a wide range of development latitude, which may show a similar level of development to that processed with a standard developer, even either with a developer having a lowered processing capacity or with a developer having a more enhanced processing capacity than that of the standard.

In both photosensitive lithographic printing plates and photoresists, there have been hitherto employed novolak resins such as phenol-formaldehyde resin or cresol-formaldehyde resin as an alkali-soluble resin employed together with the photosensitive *o*-quinonediazido compound. On the other hand, West German laid-open Patent Application (OLS) No. 26 16 992 discloses that resistance to alkali developers in the photosensitive lithographic printing plate or abrasion resistance of the coated film in the photosensitive layer could be improved by employing such a novolak resin prepared by polycondensation of phenol substituted with an alkyl group having 1 to 9 carbon atoms with formaldehyde. Also, Japanese Unexamined Patent Application No. 127553/1970 discloses that resistance to alkali developers could be enhanced as mentioned above by employing as a binder a copolycondensation novolak resin prepared by condensation of a phenol substituted with an alkyl group having 3 to 12 carbon atoms or a phenyl group; phenol, phenol derivatives substituted with methyl or a mixture thereof; and formaldehyde.

The above-mentioned two types of resins may improve said safelight property to some extent, while they are not easily soluble in alkali and a photosensitive lithographic printing plate having the photosensitive layer containing said resins shows a poor alkali-solubility when developed and could not be sufficiently developed with a lowered sensitivity when processed with a developer having a lowered developing capacity than the standard level, e.g., by exhaustion over a prolonged period of development.

Japanese Unexamined Patent Application No. 116218/1979 discloses that alkali solubility, oleophilicity and acid resistance could be improved by using a copolycondensation novolak resin prepared by condensation of a tert-alkylphenol having 4 to 8 carbon atoms and phenol or cresol

with formaldehyde, either alone or in combination with two or more thereof.

However, the resultant photosensitive lithographic printing plate employing the avobe-mentioned novolak resin has drawbacks of alkali solubility being not always satisfactory, development latitude being narrow and ball-point pen resistance being poor.

Japanese Unexamined Patent Application No. 57841/1970 discloses that alkali-solubility, chemical resistance, printing resistance and ink-receptibility could be improved with a novolak resin of the copolycondensated resin with phenol, cresol and aldehyde. However, this resin, if a weight-average molecular weight (Mw) is not more than 6000, can provide a photosensitive lithographic printing plate having a good alkali-solubility and a high sensitivity, while showing an extremely poor ball-point pen resistance and safelight property and, when processed with a developer having an enhanced developing capacity owing to raised bath temperature and so on, show a remarkable attack in image portions. Of the other hand, if said Mw is more than 6000, resistance to said developer having an enhanced capacity beyond the standard level is raised with somewhat improved safelight property, but ball-point pen resistance could hardly be improved together with a lower sensitivity or alkali-solubility.

U.S. Patent No. 4,377,631 discloses that sensitivity and resolving power could be increased in a photoresist composition by using a resin prepared by copolycondensation of *m*-cresol and *p*-cresol or *o*-cresol with formaldehyde as the resin for photoresist. However, this resin, if its melting point is less than 110 °C, can provide a photosensitive lithographic printing plate using said resin with a good alkali-solubility, but it also gives poor ball-point resistance and safelight property. If the melting point of not lower than 110 °C, safelight property may be improved to some extent, but alkali-solubility may be significantly lowered, non-image portion could not be sufficiently developed by processing with an exhausted developer and ball-point pen resistance could not be improved so well.

Japanese Patent Publication N. 23570/1979 discloses that sensitivity could be improved by employing as a resin to be contained in a photoresist composition two kinds of phenol-formaldehyde novolak resins or resol resins which have different solubility in an alkali solution of a pH value of not more than 12. However, there has been used a developer with a higher alkalinity of a pH value of up to 13 for the photosensitive lithographic printing plate using *o*-quinonediazido compounds. Therefore, when said two types of resins are applied to photosensitive lithographic printing plate, sensitivity may be improved, but the photosensitive layer or the image part in unexposed portions may be significantly attacked by an alkali developer with poor safelight property and ball-point pen resistance.

Japanese Unexamined Patent Application Nos. 101833/1982 and No. 10184/1982 disclose that chemical resistance, alkali-solubility and printing resistance could be improved by applying to a photosensitive lithographic printing plate using *o*-quinonediazido compounds a condensate of a polyhydric phenol and benzaldehyde, e.g., a resorcinol-benzaldehyde resin, a pyrogallol-benzaldehyde resin, etc., or copolycondensation resin of polyhydric phenols and acetone, e.g., a pyrogallol-resorcinol-acetone resin, etc. However, it has a drawback of poor safelight property and ball-point pen resistance.

Japanese Unexamined Patent Application No. 86046/1984 discloses that weak alkali development may be made by utilizing a condensate of a catechol or hydroquinone derivative with an aldehyde for a photosensitive composition; however, safelight property and ball-point pen resistance are still poor like the previous Japanese Application case.

Japanese Unexamined Patent Application No. 157238/1982 discloses that chemical resistance could be improved with a shortened period of burning process by applying to a photosensitive lithographic printing plate using *o*-quinonediazido compounds a novolak resin having halogenophenol units; however, development latitude is narrow and ball-point pen resistance is poor.

SUMMARY OF THE INVENTION

It is accordingly a primary object of this invention to provide a photosensitive composition which can show superior safelight property and resistance to ball-point pen, and a wide range of development latitude, without any decrease in sensitivity.

The object of this invention can be accomplished by a photosensitive composition comprising an *o*-quinonediazido compound and a novolak resin, wherein said *o*-quinonediazido compound is an *o*-naphthoquinonediazidosulfonic acid ester of a polycondensation resin of pyrogallol with acetone and has a number-average molecular weight (Mn) of 5.0×10^2 to 1.5×10^3 and a weight-average molecular weight (Mw) of 7.0×10^2 to 4.0×10^3, and said novolak resin has a weight-average molecular weight (Mw') of 6.0×10^3 to 2.0×10^4 and the ratio of said weight-average molecular weight (Mw') to a number-average molecular weight (Mn') of said novolak resin (Mw'/Mn') is 2 to 14.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The novolak resin which may be employed in this invention is a resin prepared by condensation of a phenol with formaldehyde in the presence of an acid catalyst. As the phenol, there

may be mentioned, for instance, phenol, *o*-cresol, *m*-cresol, *p*-cresol, 3,5-xylenol, 2,4-xylenol, 2,5-xylenol, carvacrol, thymol, cathecol, resorcin, hydroquinone, pyrogallol, phloroglucinol, a *p*-C_1–C_8 alkyl substituted phenol and the like. Said phenols may be employed alone or in combination with two or more thereof for condensation with formaldehyde to prepare the resin. Of these novolak resins, there may be preferably named the resin prepared by copolycondensation of at least one selected from phenol, *m*-cresol, *o*-cresol and *p*-cresol with formaldehyde: For instance, there may be mentioned a phenol-formaldehyde resin, an *m*-cresol-formaldehyde resin, an *o*-cresol-formaldehyde resin, a phenol-*p*-cresol-formaldehyde copolymer resin, an *m*-cresol-*p*-cresol-formaldehyde polycondensate resin, an *o*-cresol-*p*-cresol-formaldehyde copolycondensate resin, a phenol-*m*-cresol-*p*-cresol-formaldehyde copolycondensate resin and a phenol-*o*-cresol-*p*-cresol-formaldehyde copolycondensate resin. In the above-listed novolak resins, there may be preferably mentioned the phenol-*m*-cresol-*p*-cresol-formaldehyde resin.

A molecular weight (on a polystyrene basis) of the present novolak resin is a weight-average molecular weight (Mw) of 6.0×10^3 to 2.0×10^4, preferably 8.0×10^3 to 1.5×10^4. A ratio of said weight-average molecular weight Mw to a number-average molecular weight Mn of said novolak resin, Mw/Mn (hereinafter referred to as "degree of dispersion"), is 2 to 14, preferably 3 to 9, particularly preferably 6 to 9.

Where the present novolak resin has a weight-average molecular weight Mw of less than 6.0×10^3, there would become significantly poor a resistance to the developer having higher safelight property, ball-point pen suitability and developing capacity than the standard levels thereof (hereinafter referred to as "over-development property"). On the other hand, where said weight-average molecular weight Mw is more than 2.0×10^4, there would be lowered a developability to the developer having a lowered developing capability than the standard level thereof (hereinafter referred to as "underdevelopment property") with a reduced sensitivity, which makes development to be infeasible.

Moreover, where the degree of dispersion (Mw/Mn) is les than 2, there would be observed a reduced underdevelopment property, while there would be observed a lowered safelight property in the case where the Mw/Mn is more than 14, which results in a narrow development latitude.

A molecular weight of the resin is determined according to a gel permeation chromatography (GPC) method. A number-average molecular weight Mn and a weight-average molecular weight Mw are calculated by a method in which leveling peaks in oligomer region or linking centers of the top and bottom in the peak according to the method taught by Morio Tsuge et al in the Journal of the Chemical Society of Japan (in Japanese), PP. 800–805 (1972).

A content of the novolak resin in photosensitive compositions is preferably 30 to 95 % by weight, more preferably 50 to 85 % by weight.

Preferably, the present photosensitive composition may include two or more of the above-mentioned novolak resins. It is more preferalbe that the respective molar raito of charged phenol and *p*-cresol when combined resins are to be prepared is at least 5 % in said total resins.

The present novolak resin may be prepared, for example, according to the method as disclosed in Polym. Sci. Polym. Chem. *11*, p. 939 (1973) by P. W. Kopf and E. R. Wagner.

The o-quinonediazido compound which may be employed in this invention is a compound having at least one of *o*-quinonediazido groups, preferably an *o*-benzoquinonediazido group or an *o*-naphthoquinonediazido group and may include known compounds having various structures such as those described in detail in "Light-Sensitive Systems" by J. Kosar, John Wiley & Sons, inc., 1965, pp. 339–353. Particularly, esters or amides of various hydroxy compounds or amino compounds with *o*-naphthoquinonediazidosulfonic acid. As preferable hydroxy compounds, there may be mentioned condensed resins of a phenol with a carbonyl group-containing compound, particularly, those which can be prepared by condensation in the presence of an acid catalyst. As the phenol, there may be mentioned, for example, phenol, resorcin, cresol, pyrogallol and the like. As the carbonyl group-containing compound, there may be mentioned, for example, aldehydes such as formaldehyde or benzaldehyde and ketones such as acetone. In particular, there may be preferably named a phenol-formaldehyde resin, a cresol-formaldehyde resin, a pyrogallol-acetone resin and a resorcin-benzaldehyde resin.

As representative examples of the *o*-quinonediazido compounds, there may be named an ester of benzoquinone-(1,2)-diazidosulfonic acid or naphthoquinone-(1,2)-diazidosulfonic acid with a phenol-formaldehyde resin or a cresol-formaldehyde resin; an ester of naphthoquinone-(1,2)-diazidosulfonic acid with a pyrogallol-acetone resin as disclosed in U.S. Patent No. 3,635,709; a condensate of naphthoquinone-(1,2)-diazido-(2)-5-sulfonic acid with a resorcin-benzaldehyde resin as disclosed in Japanese Unexamined Patent Application No. 1044/1981; an ester compound of naphthoquinone-(1,2)-diazido-(2)-5-sulfonic acid with a resorcin-pyrogallol-acetone copolycondensate as disclosed in Japanese Unexamined Patent Application No. 76346/1980. As other useful *o*-quinonediazido compounds, there may be named an ester of a polyester having terminal hydroxy groups with *o*-naphthoquinone-diazidosulfonic acid as disclosed in Japanese Unexamined Patent Application No. 11750/1975; an ester of a homopolymer of *p*-hydroxystyrene or a copolymer thereof with other copolymerizable monomer with *o*-naphthoquinone-diazidosulfonic

acid and the like.

In the present photosensitive compositon, the *o*-quinonediazido compound may comprise preperably 5 to 60 % by weight, particularly preferably 10 to 50 % % by weight.

The *o*-quinonediazido compound is preferably an *o*-quinonediazidosulfonic acid ester of a polycondensation resin of a polyhydroxyphenol with a ketone or aldehyde, which has a number-average molecular weight of 4.0×10^2 to 2.0×10^3 and a weight-average molecular weight of 5.0×10^2 to 4.0×10^3. More preferable is the *o*-naphthoquinonediazidosulfonic acid ester of a polycondensation resin of pyrogallol with acetone, which has a number-average molecular weight of 5.0×10^2 to 1.5×10^3 and a weight-average molecular weight of 7.0×10^2 to 4.0×10^3.

The *o*-quinonediazidosulfonic acid ester may be prepared by dissolving a condensation resin of said phenol and said carbonyl group-containing compound in a suitable solvent, e.g., dioxane, etc., adding *o*-quinonediazidosulfonic acid chloride and then adding dropwise an alkali carbonate until an equivalent point to conduct esterification.

In said ester compound, a condensation rate of *o*-naphthoquinonediazidosulfonic acid chloride to the hydroxy group in said ester compound (% to one OH group) is preferably 20 to 80 %, more preferably 25 to 70 %, still more preferably 30 to 60 %.

A number-average molecular weight and a weight-average molecular weight of said ester compound are determined in the same manner as done for said novolak resin.

The present photosensitive composition may further comprise other additives, where nacessary, in addition to the aforesaid components. As a plasticizer, there may be mentioned various low molecular weight compounds such as phthalic acid esters, triphenylphosphates, maleic acid esters; as a coating improving agent, there may be mentioned surface active agents such as fluorine-containing surface active agents or nonion sufactants, such as, typically, ethyl cellulose polyalkylene ethers; and various print-out materials for forming a visible image upon exposure to light.

The print-out material may comprise a compound capable of forming an acid or a free radical and an organic dye which is capable of changing its original tone by interaction with the former. As the former compound, there may be mentiond, for example, an *o*-naphthoquinonediazido-4-sulfonic acid halide as disclosed in Japanese Unexamined Patent application No. 36209/1975, a trihalomethyl-(2)-pyrone or a trihalomethyl-triazine as disclosed in Japanese Unexamined patent Application No. 36223/1978, an ester compound of an *o*-naphthoquinonediazido-4-sulfonic acid chloride with a phenol or an aniline having an electron attractive substituent as disclosed in Japanese Unexamined Patent application No. 6244/1980, a halomethyl-vinyl-oxadiazole compound and a diazonium salt as disclosed in Japanese Unexamined Patent Application No. 77742/1980 and the like.

As said organic dye, there may be mentioned, triphenylmethane-, diphenylmethane-, oxazine-, xanthene-, iminonaphthoquinone-, azomethine- or anthraquinone-type dyes, typically, for example, Victoria Pure Blue-BOH (trade name; available from Hodogaya Chemical Co., Ltd.), Oil Blue β603 (trade name; available from Orient Chemical Co., Ltd.), Patent Pure Blue (trade name; available from Sumitomo-Mikuni Chemical Co., ltd.), Crystal Violet, Brilliant Green, Ethyl Violet, Methyl Green, Erythrocin B, Basic Fuchsine, Malachite Green, Oil Red, m-Cresol Purple, Rhodamine B, Auramine, 4-p-diethylaminophenyl-iminonaphthoquinone, cyano-p-diethylaminophenyl-acetanilide and the like.

Also, a photosensitive resin, which may be prepared by condensation of an oleophilic phenol-formaldehyde resin and a *p*-substituted phenol-formaldehyde resin with an *o*-quinonediazidosulfonic acid chloride is preferably added for improving an oleophilicity. The oleosensitizer may preferably comprise, 0.1 to 3 % by weight upon a total of the photosensitive composition.

A sensitizer for improving sensitivity may be incorporated into the present photosensitive composition. As the sensitizer, there may be mentioned, for example, a gallic acid derivative as disclosed in Japanese unexamined Patent Application No. 118237/1982; a 5-membered cyclic acid anhydrides, e.g., phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, maleic anhydride, succinic anhydride, pyromellitic acid, itaconic acid as disclosed in Japanese Unexamined Patent Application No. 80022/1977; a 6-menbered cyclic acid anhydride, e.g., glutaric anhydride or derivatives thereof as disclosed in Japanese Patent Application No. 11932/1983, and the like. In them, cyclic acid anhydrides may be preferable and 6-membered cyclic acid anhydrides are particularly preferable.

The present photosensitive composition may be dissolved in a suitable solvent capable of dissolving all of the above components, coated and dried onto a suitable base or support to produce, for example, a photosensitive lithographic printing plate or a photoresist.

As the solvent which may be applied, there may be named, for instance, cellosolves, e.g., methyl cellosolve, methyl cellosolve acetate, ethyl cellosolve, ethyl cellosolve acetate, etc., dimethylformamido, dimethyl sulfoxide, dioxane, acetone, cyclohexanone, trichloroethylene, methyl ethyl ketone and so on. Such solvents may be applied alone or in combination with two or more thereof.

Coating may be carried out according to well known procedures, e.g., rotary coating, wire bar

coating, dip coating, air knife coating, roll coating, blade coating, curtain coating and the like.

As a base support, over which a photosensitive layer is provided by applying the present photosensitive composition, there may be mentioned, for instance, a metal plate such as aluminum, zinc, copper, steel; a metal plate metallized or deposited with chromium, zinc, copper, nickel, aluninum, iron, etc.; a paper; a plastic film and a glass plate; a paper coated with a resin; a paper stuck with a metal foil such as aluninum; a hydrophilized plastic film and so on, with an aluminun plate being preferable.

Where an aluminum plate is used for a base of a photosensitive lithographic printing plate, surface treatment such as graining treatment, anodization treatment and, if necessary, sealing treatment may be preferably applied to the plate. There Treatments may be effected according to well-known procedures.

As the graining treatment, there may be mentiond, for example, mechanical procedures or electrolytic etching procedures. Mechanical procedures may involve, e.g., ball abrasion, blush abrasion, abrasion with liquid honing, buff abrasion and so on. Depending upon a composition of the aluminum material employed and others, there may be employed the aforesaid procedures alone or in combination therewith. Electrolytic etching is preferred.

Electrolytic etching may be carried out in a bath containing an inorganic acid, e.g., phosphoric acid, sulfuric acid, hydrochloric acid, nitric acid, etc., alone or in admixture therewith. After graining treatment, there may be, where necessary, applied desmut treatment with an aqueous solution of an alkali or acid to neutralize and washing with water.

Anodization treatment may be carried out by using as an electrolyte a solution containing one or more of sulfuric acid, chromic acid, oxalic acid, phosphoric acid, malonic acid and the like and as a positive elecrode an aluminum plate for electrolysis, Coated amount formed by positive electrode oxidation is suitably 1 to 50 mg/dm^2, preferably 10 to 40 mg/dm^2, and particularly preferably 25 to 40 mg/dm^2. Said coated amount may be determined, for instance, by dipping an aluminum plate into a phosphoric acid-chronic acid solution (prepared by dissolving 35 ml of a 85 % phosphoric acid solution and 20 g of chromium (VI) oxide in 1 liter of water) to dissolve oxidative coating and measuring changes in weight before and after dissolution of the plate coating film.

Sealing treatment may involve, illustratively, boiled water-, steam-, sodium silicate- or aqueous dichromate solution-treatments. Further, undercoating treatment with an aqueous solution of a water-soluble high polymer compound or a metal salt, e.g., zirconic fluoride may be applied to an aluminum plate base.

Moreover, a method of improving vacuum contact, wherein a printing frame is generally employed under vacuum in contacting and printing an original film to a photosenstive lithographic printing plate, may be also applicable to such a photosensitive lithographic printing plate using the present photosensitive composition. As the method for improving a vacuum contact, there may be mentioned, for example, a method to make a photosensitive layer surface uneven mechanically, a method to distribute solid powders over a photosensitive layer surface, a method to place a matting layer over a photosensitive layer surface as disclosed in Japanese Unexamined Patent Application No. 125805/1975, a method to make solid powders thermally fusion bonded over a photosensitive layer surface as disclosed in Japanese Unexamined Patent Application No. 12974/1980 and the like.

Photosensitive lithographic printing plate or photoresists to which the present photosensitive composition is applied may be utilized in the same manner as done for conventional ones previously used.

For instance, the plate may be exposed through a transparent positive film to a light source such as a super-presure mercury lamp, a metal halide lamp, a xenon lamp, a tungusten lamp and so on and then developed with an alkali developer, thereby unexposed portions solely being left on the bare surface and relief image of the positive-positive type being formed.

As the alkali developer, there may be mentioned for example, an aqueous solution of an alkali metal salt, e.g., sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium metasilicate, potassium metasilicate, sodium secondary phosphate or sodium tertiary phosphate. A concentration of the alkali metal salt is preferably 0.1 to 10 % by weight. Also, said developer may, where necessary, comprise further anionic surface active agents, amphoteric surface active agents or organic solvents, e.g., alcohols, etc.

The present invention will be more fully illustrated by way of the following Examples, but they are not contemplated to be limiting the scope of the present invention.

Example 1

An aluminum plate with a thickness of 0.24 mm was degreased in a 5 % aqueous solution of sodium hydroxide and then subjected to electrolytic etching in a 0.5 mole aqueous hydrochloric acid under the condition of a temperature of 25 °C, a current density of 60 A/dm^2 and a processing period of 30 seconds. After desmut treatment with a 5 % aqueous solution of sodium hydroxide, anodic anodization treatment was then applied in a sulfuric acid solution.

Coated film amount by anodic anodization was 27 mg/dm² as measured according to the aforesaid method. Then, sealing treatment was done by dipping it in a hot water at 90 °C.

Subsequently, a photosensitive coating liquid having the following composition was coated over the resultant aluminum support by means of a rotary coater, and then dried at 100 °C for 4 minutes to produce a photosensitive lithographic printing plate (A).

Composition of photosensitive coating liquid

1) Ester compound of naphthoquinone-(1,2)-diazido-(2)-5-sulfonic acid chloride with pyrogallol-acetone resin (number-average molecular weight Mn=1500, weight-average molecular weight Mw=1700, condensation rate 50 mole %) .... 1.6 g

2) Copolycondensation resin of phenol, *m*-, and *p*-mixed cresols and formaldehyde (molar ratio of phenol: *m*-cresol: *p*-cresol=40:36:24, Mw=9300, degree of dispersion Mw/Mn=6.2; hereinafter referred to as "Novolak resin [I]") .... 6.5 g

3) Ester compound of novolak resin prepared from *p*-tert-octylphenol and formaldehyde with naphthoquinone-(1,2)-diazido-(2)-5-sulfonic acid chloride (condensation rate 50 mol. %, Mw=1800) .... 0.164 g

4) Oil Blue β603 (trade name; available from Oriental K.K.) 0.08 g

5) Ethylene glycol monoethyl ether .... 68 g

6) Ethylene glycol monomethyl ether .... 33 g

Coated amount after dried .... about 22 mg/dm²

Molecular weight and degree of dispersion for the avobe-mentioned ester compound 1) and copolycondensation resin 2) were determined according to a gel permeation chromatography (GPC). The GPC measurement conditions are as follows:

Apparatus: Type 635 of Hitachi Ltd.; separation of column, 3 columns of Shodex A802, A803 and A804 produced by Showa Denko K.K. connected in series; temperature: room temperature; solvent: tetrahydrofuran; flow rate: 1.5 ml/min.

A calibration curve was prepared as a standard of polystyrene.

Over the so-formed photosensitive lithographic printing plate was contacted a step tablet for sensitivity measurement (Kodak step tablet No. 2 produced by Eastman Kodak Co., Ltd., a gray scale with 21 steps by a difference in density of 0.15) and the resultant plate was exposed to a light source of 2 KW metal halide lamp (Idlefin 2000 produced by Iwasaki Electric Co., Ltd.) at 8.0 mW/cm² over 70 seconds. Then, the sample was developed with a 4 % aqueous solution of potassium metasilicate at 25 °C for 45 seconds, thereby a non-image portion being completely removed to form a lithographic printing plate. Measurement of sensitivity by the gray scale with said step tablets showed 4 1/2 step was completely developed or made clear.

Then, there were prepared a developer which had a more diluted alkali concentration than that of a standard 4 % aqueous solution of potassium metasilicate, and a developer which had a more concentrated alkali level than that of the said standard, in order to study development latitude. By using the sample exposed for 70 seconds as disclosed above, there were investigated development to the developer having a lowered developing capacity (underdevelopment) and also development to the developer having an excessive developing capacity (over-development). In studying underdevelopment, development was done, respectively, with 2.1 % and 1.9 % aqueous solution of potassium metasilicate at 25 °C for 45 seconds to evaluate solubility of non-image portions. The more the photosensitive layer in non-image portions could be dissolved in said diluted developer, the better underdevelopment shall be determined to be.

On the other hand, where overdevelopment is to be studied, development was done with a 6.0 % aqueous solution of potassium metasilicate at 25 °C for 60 seconds and with a 7.2 % aqueous solution of potassium metasilicate at 25 °C for 90 seconds, respectively; the solid step number (i.e., the minimum step number where a photosensitive layer completely remains in the gray scale of said step tablet) was measured and then the difference between said step number and the solid step number of a standard development (with a 4 % aqueous solution of potassium metasilicate at 25 °C for 45 seconds) was determined. The smaller such solid step number difference is so as to be close to the standard development, the better overdevelopment shall be regarded as. Good development latitude is meant to be good in both underdevelopment and overdevelopment.

For studying ball-point pen resistance, on the aforesaid photosensitive lithographic printing plate (A) before exposure and development were drawn lines by means of three types of ball-point pens, i.e., the ball-point pens [I] (ZEBRA N5100 black, produced by Zebra K. K.), [II] (GOLF blue, produced by Tombow Enpitsu K.K.) and [III] (Pilot BS-blue, the Pilot Pen Co., Ltd.). After standing for 10 mintues, said standard development was done without exposure. Ball-point pen resistance was evaluated by determination of attacked levels in the photosensitive layer after handwritten with 3 rankings.

For studying safelight property, said photosensitive lithographic printing plate (A) before exposure and development was exposed to a white color fluorescent lamp with 310 1x. for 10 mintues to produce optical fog and then subjected to said standard development. A film

reduction rate in the photosensitive layer was determined. The film reduction rate is meant to be a value showing reduction level in a film thickness where a film thickness of the photosensitive layer in the photosensitive lithographic printing plate developed without optical fog is compared with the thickness of the layer developed with optical fog. Therefore, the less such a value is, the better safelight property is.

Also, for studying decrease in printing resistance with optical fog, said photosensitive lithographic printing plate (A) in contact with a positive original film as mentioned above was exposed and optical fog was produced as above by means of a white color fluorescent lamp. Subsequent standard development was effected to form a lithographic printing plate [I]. On the other hand, another lithographic printing plate [II] was prepared in the same processing manner as above without applying any optical fog. The two lithographic printing plates [I] and [II] were set together in an offset printing machine (HAMADASTAR 900CDX, produced by Hamada printing press manufacture company Co., Ltd.) to conduct printing. End point of printing resistance was determined to be the point where a solid part in image portion was peeled off and printing could be no longer done.

The results of sensitivity, development latitude, ball-point pen resistance and safelight property are summarized in the following Table 1.

Comparative Example 1

Following the same procedures as in Example 1 except that the under-mentioned novolak resin [II] was used instead of the novolak resin [I] in the photosensitive coating liquid, there was prepared a photosensitive lithographic printing plate (B).

Novolak resin [II]

Copolycondensation resin of phenoland *m*- and *p*-mixed cresols with formaldehyde (molar ratio of phenol:*m*-cresol:*p*-cresol=40:36:24, Mw=1500, Mw/Mn=6.2)

Namely, novolak resins [I] and [II] are the same in composition and degree of dispersion and different only in Mw.

Coated weight after dried .... about 22 mg/dm^2.

The photosensitive lithographic printing plate (B) was evaluated in the same manner as in Example 1 for sensitivity, development latitude, ball-point pen resistance and safelight property. The results are shown in Table 1.

Comparative Example 2

Following the same procedures as in Example 1 except that the under-mentioned novolak resin [III] was used instead of the novolak resin I in the photosensitive coating liquid, there was prepared a photosensitive lithographic printing plate (C).

Novolak resin [III]

Copolycondensation resin of phenol and *m*- and *p*-mixed cresols with formaldehyde (molar ratio of phenol:*m*-cresol:*p*-cresol=40:36:24, Mw=9320, Mw/Mn=15)

Namely, novolak resins [I] and [III] are approximately the same in composition and weight-average molecular weight, but different in degree of dispersion.

Coated weight after dried .... about 22 mg/dm^2

The photosensitive lithographic printing plate (C) was evaluated in the same manner as in Example 1 for sensitivity, development latitude, ball-point pen resistance and safelight property. The results are shown in Table 1.

Comparative Example 3

Following the same procedures as in Example 1 except that the under-mentioned two novolak resins (a total of 6.5 g) were used instead of the novolak resin [I] in the photosensitive coating liquid, there was prepared a photosensitive lithographic printing plate (D).

1) Copolycondensation resin of phenol, *p*-tert-butylphenol and formaldehyde (molar ratio of phenol:*p*-tert-butylphenol=50:50, prepared in the same manner as in Example 1 of Japanese Unexamined Patent Application No. 127553/1980, Mw=5000, Mw/Mn=4.5) .... 3.25 g

2) Phenol-formaldehyde novolak resin (Mw=21000, Mw/Mn=17) .... 3.25 g

Coated weight after dried .... about 22 mg/dm^2

The photosensitive lithographic printing plate (D) was evaluated in the same manner as in Example 1 for sensitivity, development latitude, ball-point pen resistance and safelight property. The results are given in Table 1.

Comparative Example 4

Following the same procedures as in Example 1 except that the under-mentioned novolak resin was used instead of the novolak resin [I] in the photosensitive coating liquid, there was prepared a photosensitive lithographic printing plate (E).

Novolak resin

Copolycondensation resin of *m*-cresol and *p*-cresol with formaldehyde (molar ratio of *m*-cresol:*p*-cresol=50:50, prepared in the same manner as in Synthesis Example 1 of West German Patent Laid-open Application (OLS) NO. 26 16 992, Mw=1800, Mw/Mn=1.4).

Coated weight after dried .... about 22 mg/dm²

The photosensitive lithographic printing plate (E) was evaluated in the same manner as in Example 1 for sensitivity, development latitude, ball-point pen resistance and safe light property. The results are shown in Table 1.

Comparative Example 5

Following the same procedures as in Example 1 except that the under-mentioned novolak resin was used instead of the novolak resin [I] in the photosensitive coating liquid, there was prepared a photosensitive lithographic printing plate (F).

Novolak resin

Copolycondensation resin of phenol and *p*-tert-butylphenol with formaldehyde (weight ratio of phenol:*p*-tert-butylphenol=60:40, as disclosed in Synthesis Example 1 of Japanese Unexamined Patent Application No. 116218/1979, Mw=4500, Mw/Mn=4.0).

Coated weight after dried .... about 22 mg/dm²

The photosensitive lithographic printing plate (F) was evaluated in the same manner as in Example 1 for sensitivity, development latitude, ball-point pen resistance and safelight property. The results are shown in Table 1.

Table 1

	Sensitivity (step number cleared)	Development latitude				Ball-point pen resistance			Safelight property	
		Overdevelopment		Under development					Film reduction rate (%)	Printing resistance reduction rate (%)
		6.0% 25°C/60"	7.2% 25°C/90"	2.1%	1.9%	I	II	III		
Example 1	4 1/2	2.0	3.0	○	○	A	A	A	8	15
Comparative Example 1	5	5.0	-	○	○	C	B	C	75	90
Comparative Example 2	4 1/2	3.0	5.0	○	△	C	B	B	50	75
Comparative Example 3	3	1.0	2.5	X	X	B	A	B	10	20
Comparative Example 4	3 1/2	1.5	2.5	△	X	B	A	B	13	25
Comparative Example 5	2 1/2	1.0	2.0	X	X	B	A	B	10	18

On the above Table 1, the letter "A" shows slight attack in image portion, the letter "B" shows slight attack and slightly exposed grained surface in the support beneath the photosensitive layer, and the letter "C" shows remarkable attack and completely exposed grained surface in the support beneath the photosensitive layer.

In the underdevelopment column, the open circle symbol (O) shows complete dissolution and removal of the photosensitive layer in non-image portion, the open trianglesymbol (Δ) shows partial retention of the photosensitive layer, and the X-shaped symbol (X) shows little dissolution of the photosensitive layer.

In the overdevelopment column, the indicated value is meant to show difference in solid step number with standard development and the symbol (—) shows remarkable attacked image portion to indicate too poor overdevelopment to hardly determine solid step number.

The results from the above Example and Comparative Examples have revealed the following points: Namely, when Example 1 is compared with Comparative Example 1, overdevelopment, ball-point pen resistance and safelight property are remarkably lowered in the novolak resins of the same composition used, if said weight-average molecular weight Mw is not more than 6,000 even with the same degree of dispersion of not more than 14 in both resins. Comparison of Example 1 with Comparative Example 2 shows that overdevelopment and safelight property are greatly reduced if both novolak resins of the same composition used have a degree of dispersion of not less than 14 even with the same weight-average molecular weight of not less than 6,000.

Performance of a photosensitive lithographic printing plate could not be evaluated upon any one property solely, but should be generically rated upon several properties. The photosensitive lithographic printing plates (B) to (F) as above have an outstanding disadvantage with regard to at least any one of properties in Table 1; namely, Comparative Example 1 showed poor overdevelopment, ball-point pen resistance and safelight property, Comparative Example 2 shows poor safelight property and overdevelopment and Comparative Examples 3 to 5 showed lower sensitivity and poor underdevelopment.

The present photosensitive lithographic printing plate (A) of the above Example 1 did not show any serious disadvantages, i.e., it showed superior over-and under-development, wide development latitude as well as, generically, uniform, superior sensitivity, ball-point pen resistance and safelight property.

Example 2

Following the same procedures as in Example 1 except that a photosensitive coating liquid of the following composition was coated on the aluminum support prepared in Example 1 and was then dried, there was prepared a photosensitive lithographic printing plate (G).

Composition of photosensitive coating liquid

1) Ester compound of naphthoquinone-(1,2)-diazido-(2)-5-sulfonic acid chloride with *m*-cresol-formaldehyde novolak resin (condensation rate=25 mol. %, Mn=1200, Mw=1800) .... 2.9 g
2) Copolycondensation resin of *o*-, *m*- and *p*-mixed cresols and formaldehyde (weight ratio of *m*-cresol:*p*-cresol:*o*-cresol=70:20:10, Mw=9200, Mw/Mn=8.0, melting point=83 °C) .. 5.3 g
3) Victoria Pure Blue-BOH (trade neme; produced by Hodogaya Chemical Co., Ltd.) ...... 0.08 g
4) Ethylene glycol monoethyl ether .... 100 g

Coated weight after dried .... about 22 mg/dm²

Molecular weight and degree of dispersion of said ester compound 1) and copolycondensation resin 2) were determined in the same manner as in Example 1. Melting point was measured by means of a melting point measurement apparatus Buchi 510 produced by BUCHI Co. Ltd.

The thus obtained photosensitive lithographic printing plate (G) was evaluated in the same manner as in Example 1 for sensitivity, development latitude, ball-point pen resistance and safelight property. The results are summarized in Table 2.

Comparative Exampel 6

Following the same procedures as in Example 1 except that the following novolak resin was used instead of the copolycondensation resin 2) in Example 2, there was prepared a photosensitive lithographic printing plate (H).

Novolak resin

Copolycondensation resin of *o*-, *m*- and *p*-mixed cresols with formaldehyde (weight ratio of *m*-cresol:*p*-cresol:*o*-cresol=70:20:10, Mw=25000, Mw/Mn=8.0, melting point=143 °C, as synthesized in the same manner as in Example 2 of U.S. Patent No. 4,377,631) 5.3 g

Coated weight after dried ....

The photosensitive lithographic printing plate (H) was evaluated in the same manner as in Example 1 for sensitivity, development latitude, ball-point pen resistance and safelight property. The results are shown in Table 2.

Comparative Example 7

Following the same procedures as in Example 1 except that the following novolak resin was used instead of the copolycondensation resin 2) in Example 2, there was prepared a photosensitive lithographic printing plate (I).

Novolak resin

Copolycondensation resin of *o*-, *m*- and *p*-mixed cresols with formaldehyde (weight ratio of *m*-cresol:*p*-cresol:*o*-cresol=70:20:10, Mw=25,000, Mw/Mn=15, melting point=100 °C) .. 5.3 g

Coated weight after dried .... about 22 mg/dm²

The photosensitive lithographic printing plate (I) was evaluated in the same manner as in Example 1 for sensitivity, development latitude, ball-point pen resistance and satellant property.

The results of Example 2 and Comparative Example 6 and 7 are also shown in Table 2.

Table 2

	Sensitivity (step number cleared)	Development latitude				Ball-point pen resistance			Safelight property	
		Overdevelopment		Under development					Film reduction rate (%)	Printing resistance reduction rate (%)
		6.0% 25°C/60"	7.2% 25°C/90"	2.1%	1.9%	I	II	III		
Example 2	4	1.5	2.5	○	○	A	A	A	5	10
Comparative Example 6	2 1/2	1.0	1.5	X	X	B	A	B	10	20
Comparative Example 7	3	2.5	3.5	△	△	B	B	B	30	50

In the Table 2, meanings of the symbole and values are as defined above with regard to Table 1.

As apparent from comparison of Example 2 with Comparative Example 6, underdevelopment and sensitivity are remarkably lowered even in the novolak resins of the same composition and the same degree of dispersion, if said weight-average molecular weight is not less than

As also apparent from comparison of Example 2 with Comparative Example 7, both overdevelopment and underdevelopment are somewhat lowered to provide a narrow development latitude, with a lowered safelight property, even in novolak resins of the same composition, if said degree of dispersion is more than 14 and said weight-average molecular weight (Mw) is not less than 2.0×10^4.

Following the same procedures as in Example 1 except that the following novolak resin was used instead of the copolycondensation resin 2) in Example 2, there was prepared a photosensitive lithographic printing plate (J).

Novolak resin

Copolycondensation resin of *m*- and *p*-mixed cresols with formaldehyde (molar ratio of *m*-cresol:*p*-cresol=90:10, Mw=6500, Mw/Mn=4.5) .... 5.3 g

Coated weight after dried .... about 22 mg/dm²

The photosensitive lithographic printing plate (J) was evaluated in the same manner as in Example 1 for sensitivity, development latitude, ball-point pen resistance and safelight property.

As a result, sensitivity is so high that 4 steps are cleared in a gray scale of a step tablet. As to overdevelopment, difference in solid step numbers was 2.0 under the condition of a [illegible] % aqueous solution of potassium metasilicate at 25 °C for 60 seconds, while difference in solid step numbers was 3.5 under the condition of a 7.2 % aqueous solution of potassium metasilicate at 25 °C for 90 seconds. As to underdevelopment, solubility of the open circle symbol (○) and of the open triangle symbol (△) as in Table 1 was observed, respectively, under the conditions of 2.1 % and 1.9 % aqueous solutions of potassium metasilicate at 25 °C for 45 seconds. Ball-point pen resistance was B for the said ball-point pen (I) and A for the ball-point pens (II) and (III). Safelight property was 12 % for film reduction rate and 20 % for printing resistance reduction rate.

The photosensitive lithographic printing plate (J) showed generically favourable performance with regard to sensitivity, development latitude, ball-point pen resistance and safelight property [illegible]

As apparent from the above, the photosensitive composition of this invention, containing the novolak resin having a specific weight-average molecular weight Mw and a specific degree of dispersion Mw/Mn, has improved resistance to an oily ball-point pen employing an organic solvent as solvent for ink and safelight property without reduction of sensitivity, has excellent property in under- and over-development, and has a wide development latitude.

1. A photosensitive composition comprising an *o*-quinonediazido compound and a novolak resin, wherein said *o*-quinonediazido compound is an *o*-naphthoquinonediazidosulfonic acid ester of a polycondensation resin of pyrogallol with acetone and has a number-average molecular weight (Mn) of 5.0×10^2 to 1.5×10^3 and a weight-average molecular weight (Mw) of 7.0×10^2 to 4.0×10^3, and said novolak resin has a weight-average molecular weight (Mw') of 6.0×10^3 to 2.0×10^4 and the ratio of said weight-average molecular weight (Mw') to a number-average molecular weight (Mn') of said novolak resin (Mw'/Mn') is 2 to 14.

2. The photosensitive composition according to Claim 1, wherein said novolak resin is a resin prepared by copolycondensation of at least one selected from the group consisting of phenol, *m*-cresol and *p*-cresol with formaldehyde.

3. The photosensitive composition according to Claim 2, wherein said novolak resin is a resin prepared by copolycondensation of phenol, *m*-cresol and *p*-cresol with formaldehyde.

4. The photosensitive composition according to Claim 1, wherein the weight-average molecular weight of said novolak resin (Mw') is [illegible].

5. The photosensitive composition according to Claim 1, wherein the ratio of the weight-average molecular weight (Mw') to the number-average molecular weight (Mn') of said novolak resin (Mw'/Mn') is [illegible].

6. The photosensitive composition according to Claim 4, wherein the ratio of the weight-average molecular weight (Mw') to the number-average molecular weight (Mn') of said novolak resin [illegible].

7. The photosensitive composition according to Claim 1, wherein the content of said novolak resin is [illegible] % by weight.

8. The photosensitive composition according to Claim 7, wherein the content of said novolak resin is 50 to 85 % by weight.

9. The photosensitive composition according to Claim 1, wherein said *o*-quinonediazido compound is an *o*-naphthoquinonediazidosulfonic acid ester of a polycondensation resin of pyrogallol with acetone and an *o*-naphthoquinonediazidosulfonic acid chloride.

10. The photosensitive composition according to Claim 9, wherein the condensation rate of the *o*-naphthoquinonediazidosulfonic acid chloride to the OH group in the *o*-naphthoquinonediazidosulfonic acid ester is 20 to 80 %.

11. The photosensitive composition according to Claim 10, wherein said condensation rate is 25 to 70 %.

12. A photosensitive composition substantially as described in any one of Examples 1 to 3.

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